

04.6-10 HYDROGEN BONDING AND MELTING CHARACTERISTICS OF WATER-RICH SALTHYDRATES : NEUTRON DIFFRACTION DATA ON SILICATES  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot n\text{H}_2\text{O}$ ,  $n = 4, 5, 7, 8$ .  
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Sodiumsilicate hydrates  $\text{Na}_2[\text{SiO}_2(\text{OH})_2] \cdot n\text{H}_2\text{O}$ ,  $n=4, 5, 7, 8$  have the unique monomeric tetrahedral  $[\text{SiO}_2(\text{OH})]^{-2}$ -anion in common. Different amounts of  $n$  water molecules enter the structure through different arrangements of dominating octahedral aquo-complexes  $[\text{Na}(\text{O}, \text{H}_2\text{O})_6]^{+1}$  sharing corners or edges. From complete neutron diffraction data we reveal our approach to special features in hydrogen bonding, which are in common with all 4 individual hydrate phases. Tetrahedral coordination dominates the hydrate water molecules in all 4 structures besides some distinct fivefold coordinated oxygens. From bond length/bond strength correlations we find a corresponding harmonicity in bond strengths reaching the (water) oxygen coordination centers from all types of ligands ( $-\text{H}, \dots, \text{H}, \text{Na}^+$ ).

The complete structural data, especially concerning hydrogen positions, also allows for reference standards on (MAS) $^{29}\text{Si}$ -NMR-analytical data which is available for the crystalline phases as well as for the super-cooled melts.

This study is part of a general approach to deeper understanding of  $\text{H}_2\text{O}-\text{X}(\text{O}, \text{OH})_4$  interactions in 3-dimensional icelike networks, which show up from crystalline but also disordered glasslike solids, gels or non-Newtonian liquids. We are especially interested in the structural background data of congruently melting water rich salt-hydrates. The given silicate hydrates belong to the very rare hydrates which melt congruently, definitely and which form super-cooled melts of non-Newtonian character.

04.6-11 HYDROXYSODALITE HYDRATES  
 $\text{Na}_6[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$  : TEMPERATURE-INDUCED DYNAMICS AND ORDERING OF  $\text{OH}/\text{H}_2\text{O}$  - CONSTITUENTS DURING DECOMPOSITION AND EXCHANGE REACTIONS. By S. Luger and J. Felsche, Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz, FRG.

Samples of different  $\text{H}_2\text{O}$ -content from large scale synthetic programs have been investigated by means of X-ray/neutron diffraction and thermoanalytical studies. There is strong evidence of OH-centering in hydroxysodalites  $\text{Na}_6[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . The OH-groups center the  $\text{Na}_4$ -tetrahedra within the cubo-octahedral framework-structure corresponding to C1 in common sodalites.

Oxygens of the hydroxyl-groups are located on position 2a and protons on position 8e of space group  $\text{P}\bar{4}3\text{n}$  statistically, yielding OH-bond lengths of 1.07 Å at 8K in hydroxysodalite ( $a=8.73\text{Å}$ ) from neutron powder diffraction data. Water molecules up to  $n=8$  enter the interface between the  $\text{Na}_4$ -tetrahedron and oxygens of the  $[\text{Al}, \text{SiO}_4]^{-}$ -framework on position 8e or 24i with corresponding increase of the cell volume.

There is another type of hydroxysodalite hydrate  $\text{Na}_6[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ,  $n \leq 4$  from elevated pressure (>400 bar) and temperature (200-500°C) conditions. This type reveals complex organization of  $\text{OH}/\text{H}_2\text{O}$ -groups on position 24i of space group  $\text{P}\bar{4}3\text{n}$  as favored in the model given by HASSEN & GRUNDY (1983) or GALITSKII et al. (1974).

We observe an exothermic reaction at about 150 K from freezing the  $\text{OH}/\text{H}_2\text{O}$  thermal motion probably on running this type in DSC-experiments down to 100 K. At temp. ~525 K another structural phase transition occurs upon heating at open system conditions. Fundamental reorganization of  $\text{OH}/\text{H}_2\text{O}$  constituents starts as soon as hydrate water concentration is lowered to  $n < 2$   $\text{H}_2\text{O}$ . (Al/Si) order/disorder phenomena probably affect this phase transition. From exchange experiments a less basic type of sodalite  $\text{Na}_6[\text{AlSiO}_4]_6 \cdot n\text{H}_2\text{O}$   $n \leq 8$  is obtained.